

Competitive Hydrogen Bonding in Solutions of Temperature-Sensitive Polymers in Mixed Solvents

Fumihiko Tanaka¹, Tsuyoshi Koga¹, Françoise M. Winnik²,

¹Kyoto University, Japan

²University of Montreal, Canada

Temperature-sensitive water-soluble polymers, such as poly(ethylene oxide) (PEO) and poly(*N*-isopropylacrylamide) (PNIPAM), exhibit peculiar conformational changes in water upon addition of a second water-miscible solvent such as methanol, tetrahydrofuran, or dioxane. Although the second solvent is a good solvent for the polymer, polymer chain collapses in certain compositions of mixed solvent, followed by the eventual reswelling under majority of the second solvent[1]. The tendency for phase separation is strongly enhanced by the presence of the second solvent. For instance, the LCST of aqueous PNIPAM solutions shifts to lower temperature when methanol is added[2][3]. The temperature drop is the largest, from 31.5 °C down to -7 °C, for specific molar fraction $x_m = 0.35$ of methanol[3]. This enhanced phase separation in mixed good solvents is known as *cononsolvency*[3]. Cross-linked PNIPAM gels also are known to collapse sharply in water in the presence of methanol, at around $x_m = 0.3$, and gradually recover their swollen state with increasing methanol content[4].

We propose a new mechanism to elucidate the peculiar properties of cononsolvency by introducing the concept of competitive hydrogen bonds: water and methanol strongly compete with each other to form hydrogen bonds with the polymer chain, and as a result the total number of hydrogen bonds per chain becomes minimum for the composition of mixed solvents at which the competition is the highest[5]. Such an effect of competing hydrogen bonds is nonlinearly amplified when the hydrogen bonding of both components is cooperative, i.e., when there is strong positive correlation between the nearest-neighboring bound solvent molecules within the same species and negative correlation between those of different species[5].

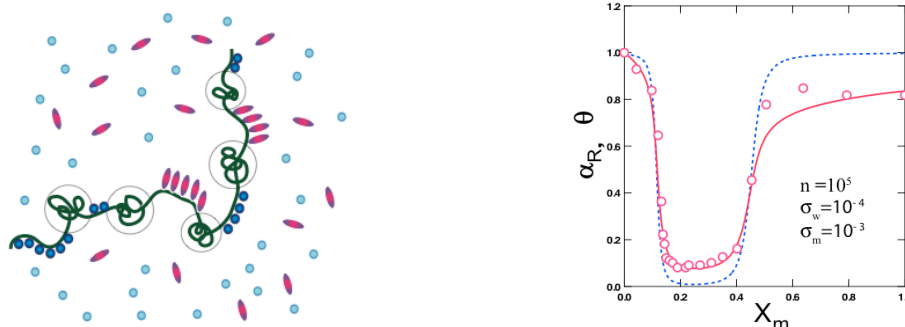


Fig.1:

[Left] Competitive hydrogen bonding on the PNIPAM chain in mixed solvent of water and methanol. [Right] Reentrant coil-to-globule-to-coil transition with methanol content. Theoretical mean end-to-end distance (solid line) is compared with the experimental data (circles) together with the total coverage (broken line).

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